—Communication—

In situ Ac Impedance Measurement during Galvanostatic Deposition and Dissolution of Lithium

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Received November 9, 1993 ; Accepted January 5, 1994

Introduction

Recently, a rechargeable lithium battery is noticed as candidates for high performance batteries. The evaluation and development of lithium anode are one of the most important point due to its dendritic deposition and the side reaction between electrolyte solution and the anode. The ac impedance measurement in the open circuit potential is one of the powerful method for evaluation of the electrode in cell^{1,2)}. However, for further evaluation of the electrode, it is very useful to operate *in-situ* ac impedance measurement during charging or discharging process of cell or battery. A few papers were published for the ac impedance measurement during galvanostatic polarization^{3,4)}. In this communication, we propose it for evaluating lithium anode charging and discharging process and discuss whether the *in-situ* method is more effective than the *ex-situ* one.

Experimental

Reagent grade propylene carbonate (PC) with 1.0 mol dm⁻³ LiClO₄ was used as electrolyte solution. Charging and discharging were measured with a working electrode of lithium deposited on nickel substrate, and a reference electrode of Li/Li⁺. The *in-situ* ac impedance measurement was carried out during the cycle of galvanostatic charging and discharging. The cycle was operated according to the procedure proposed by Koch et al.,⁵⁾ that is, lithium deposited at 1 mA cm⁻² and 1 C cm⁻² was dissolved and deposited at 0.2 C cm⁻² and the same current density. The ac current of 10 μA (zero to peak) was applied to the electrochemical cell with dc current by a galvanostat (Hokuto Denko HA-501G) equipped to a computer and potential response was analyzed by a

frequency response analyzer (NF Electric Instruments FRA S-5720C). The frequency range was covered from 10 Hz to 20 kHz. All measurements were performed under a dry argon gas atmosphere.

Results and Discussion

Figure 1 shows Cole-Cole plots obtained by the *in-situ* impedance measurement during galvanostatic Li deposition process at 1 mA cm⁻². The impedance spectra display semi-circles in higher frequency region, representing the electrode reaction during charging. The measurement during the cycle is expected to enable to avoid the time dependence of the R_{ct} value due to the measurement after the stop of the reaction. The charge transfer resistance (R_{ct}) due to Li deposition is estimated from the diameter of the semi-circle²⁾. The value is plotted against the deposition charge of Li as shown in Fig.1(b) with results of the *ex-situ* impedance measured at the open circuit potential by the superposition of the ac voltage. It is

Fig.1 *In-situ* impedance measurements for electrodeposited lithium during galvanostatic charging at 1 mA cm⁻². (a) Cole-Cole plots (b) The dependence of charge transfer resistance (R_{ct}) on deposition charge.

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Key words; Ac impedance measurement, Ac current, *In-situ* measurement, Rechargeable lithium battery

appeared that the influence of the overpotential for the charging on the change of R_{ct} value obtained by the *in-situ* measurement is small, since the change of the overpotential is small. It is difficult to determine the origin of the difference, though the difference is small, between the values obtained by the *in-situ* and *ex-situ* measurements, since the value is influenced by the many factors, such as the overpotential, the products of the side reaction, the surface morphology and so on. The change of R_{ct} determined with the *in-situ* measurement against deposition charge shows the same tendency as that obtained by the *ex-situ* one.

Figure 2 shows the results of the *in-situ* impedance measurements for each cycle of charging and discharging processes. In Figs.2(a) and (b), impedance spectrum for charging is similar to that for discharging. On the other hand, the spectrum for charging in Fig.2(c) becomes different from that for discharging, and both R_{ct} values for charging and discharging become much larger than the values in Figs.2(a) and (b). The behavior is more clearly shown in Fig.3, where the R_{ct} with the electric double layer capacitance (C_{dl}) and the time constant ($\tau = R_{ct} \cdot C_{dl}$) are shown. The three factors begin to change in the cycles when the life in the anode approaches to the end, that is, the discharge potential reaches at 1 V vs. Li/Li⁺, and after the cycles the R_{ct} and the τ sharply increase and the C_{dl} decreases. These results showed that the conditions in lithium anode change about the end of the life of the anode. Therefore, it is proved that the *in-situ* ac impedance measurement is the effective method to trace the change of the conditions in the anode during the operation.

Conclusion

When the cycles of charging and discharging processes at 1 mA cm⁻² approach to the end of the life in the anode, the charge transfer resistance changes drastically. Thus, the *in-situ* ac impedance measurement during galvanostatic polarization is proved to be very effective for tracing and quickly evaluating the conditions of the lithium anode during the processes.

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Fig.2 *In-situ* impedance spectra in each cycle at 1 mA cm⁻² and 1 C cm⁻².

Fig.3 Variations of charge transfer resistance (R_{ct}), electric double layer capacitance (C_{dl}), and time constant (τ) with cycle number during galvanostatic charging and discharging processes.